

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Alumina Refractories

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to alumina refractories and more particularly to alumina refractories formed by the *in situ* oxidation of aluminium and aluminium alloy shapes.

In our British Patent Specification No. 989,005 we have described the production of refractory materials having a continuous integral skeleton by the *in situ* oxidation of metal shapes in the presence of a fluxing agent. During the oxidation a crystalline filler refractory, that is, a material which will diffract X-rays in a discrete manner, may be present. In our co-pending British Patent Application (Serial No. 1058164) No. 5653/64 we have described the production of alumina refractories with continuous integral skeletal structures made up of cell walls or shells which are interconnected with each other.

We have also discovered that the discrete elements of the integral skeletal structure, namely, the cell walls or shells are also new and useful structures. These discrete elements are made by oxidising an aluminium shape in the presence of a fluxing agent so that it does not fuse to or become integral with another element. This is conveniently carried out by reacting aluminium particles (and flux) in a refractory diluent such as powdered magnesia, alumina or the like and separating the particles from the diluent. The concentration of the aluminium must

be less than that required to give a skeletal structure under the firing conditions used (as described in Application No. 5653/64 (Serial No. 1058164). The firing temperature must be below that causing an appreciable amount of bonding of the diluent in order that the discrete particles can be recovered. Alternatively, the particle may be oxidized singly as by hanging a 5-mil diameter aluminium filament coated with sodium silicate in a furnace and heating the same at 850° C. for four hours.

The fully converted discrete particles are hollow with an interior void or cell corresponding in shape and size to the original metal. The wall is composed of a dense (density function of 0.5 to 1.0) crystalline continuum of fine grain alpha alumina, a compound of alumina and another oxide or solid solution of an oxide in a compound of alumina and another oxide. The wall has a thickness of between about 0.3 mil and the diameter of the enclosed pore or cell. Particles of the diluent used may be occluded within the wall. The shape of the particle will correspond roughly to the shape of the starting material. Using spheres of aluminium the discrete products will be approximately spherical in shape with a diameter of between about 10 and 300 mils. When using elongated forms as fibre and foil, the length is preferably less than 2 or 3 inches.

In more detail, each hollow particle comprises a shell of crystalline refractory material surrounding a void of 0.5 to 200 mils in diameter, the crystalline refractory being selected from the group consisting of alpha-alumina, compounds and solid solutions of alumina and at least one other metal oxide, and solid solutions of at least one metal oxide in a compound of alumina and at least one other metal oxide, there being at least 30% by

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- weight of alumina in said crystalline refractory, the grains in said crystalline refractory exhibiting an average grain size of less than 8 microns and a density function of 0.5 to 1.0, the particle containing 0 to 81% by weight elemental aluminium based on the weight of the particle, the aluminium if present being within the void and/or dispersed in the crystalline refractory.
- The process for their production comprises oxidising aluminium or aluminium alloy shapes in a refractory diluent in the presence of a fluxing agent in an amount equivalent to 0.02 to 20% based on the weight of aluminium present in said shapes, and, after the oxidation has been completed, separating the hollow particles from the refractory diluent, the aluminium or aluminium alloy shapes having one dimension of at least 7 mils, a second dimension of at least 0.5 mils and a third dimension of from 0.5 to 200 mils, the fluxing agent being in contact with said shapes and being selected from the oxides of the alkali metals, the alkaline earth metals, vanadium, chromium, molybdenum, tungsten, copper, silver, zinc, antimony and bismuth and precursors of said oxides, the firing conditions employed and the amount of said shapes with respect to the refractory diluent being such that during the firing and oxidation the shapes remain separated from one another.
- The particles are strong and have a high resistance to crushing so that they can be used as a loose insulating fill, or as reinforcements for plastics, glasses and metals.
- The discrete particles containing up to about 81% preferably between 5 and 81, residual aluminium in the central void or as small (about 1 micron or less) inclusions in the wall itself are particularly useful. An aggregation of such particles can be fired in air to yield skeletal products. This firing process is much less critical than that used for making skeletal products directly from aluminium particles since the occurrence of a disruptive exotherm or the exudation of aluminium is not likely to occur. Thus mixtures containing such particles, temporary binders, and filler refractories as desired are useful for ramming mixtures, refractory castables, and moulding mixtures for all types of products.
- Granular and non-granular metal shapes may be employed, e.g., funicular, acicular or pellicular, which may be derived from structures such as a filament, continuous fibre, staple, yarn, hair, floc, sliver, shred, shaving, splinter, paring, film, foil, ribbon or the like.
- The grains in the crystalline structure have a density function (i.e., an average ratio of perimeter in contact with other grains to the total perimeter under consideration) of from about 0.5 to 1.0.
- In order that the invention may be more fully understood the following example is given by way of illustration only. In this example, all mesh sizes are U.S. Standard.
- EXAMPLE**
- Aluminium particles (grain ingot, 30/60 mesh) are wetted with a 2% solution of sodium acetate in alcohol and the excess liquid drained off. One volume (75 grams) of the treated metal is thoroughly mixed with 10 volumes (835 grams) of dead burned magnesite—200 mesh, the mixture is poured into an alumina crucible and the crucible slowly heated in an oven to 1100° C. at which temperature it is held for 24 hours. The cool mixture is screened through a 100 mesh screen to remove the unreacted magnesia.
- The coarse particles retained by the screen weigh 330 grams (bulk volume of 310 mil), are roughly spherical in shape and have a large spherical pore or void (about 10 to 23 mils in diameter) in each particle. X-ray diffraction data shows the particle to be composed of approximately equal amounts of MgO and spinel.
- When the magnesia is replaced with an equal volume of alumina (~100 mesh) similar products are obtained composed of dense, fine grain alumina with unreacted aluminium in the central cell and in micropores of the wall surrounding the cell.
- While Applicant does not wish to be bound by any particular theory, it is believed that, under the conditions of the oxidation the fluxing agents applied to the surface of the metal particles act to release the protective oxide coating which is characteristic of the aluminium, as rapidly as these coatings form thereby permitting progressive oxidation. In addition to promoting the release of the protective oxide coatings from the metal surfaces, the fluxing agent also appears to act as an oxidation transfer agent, thereby hastening the oxidation process. When size and density of metal particles in the green form permits, the simultaneous production and release of the protective oxide coating from each particle source tends to diffuse one into another, thereby providing a mutual molecular intra-distribution of oxide that results in a self-bonded final structure. During the process, the oxidised form of the nominal element of the fluxing agent is at times diffused through the metal oxide which is formed "in situ". At other times the fluxing agent is lost to the atmosphere during the firing. In certain combinations of metal and refractory fillers, chemical reaction occurs between the materials fired to produce spinels for example.
- As previously pointed out, prior to heating the shaped metal aggregate particles in an oxidizing atmosphere, the surfaces of the aggregate particles are intimately contacted with a fluxing agent as previously identified.

- The agent may be applied to the surface of the metal particles prior to their aggregation or at any other time prior to the final heating operation. The agent may be applied dry, 5 in solution, as a gas or as a melt. The manipulative technique of contacting the metal surface with it is not critical. Thus it may be powdered or sprayed upon the metal, or the metal may be dipped in a solution of 10 the agent or its melt or powder. It is conveniently done using a concentrated aqueous solution or slurry. The use of pressure and/or vacuum to assist in uniform and complete distribution of the agent over the particle 15 surfaces is often advantageous. Furthermore, when using dilute solutions, the addition of a thickener such as sodium carboxy methyl cellulose may be advantageous.
- The fluxing agent is calculated on the basis 20 of the metal oxide that it forms in those cases where a metal oxide precursor is used. The metal oxide or hydroxide can vary in amount from 0.02 to 20% based on the total weight of the aluminium in the shapes. Preferably from about 0.2 to 5% is used. Higher concentrations of fluxing agent may be employed but are generally avoided, unless the fluxing agent also acts as a filler refractory, to prevent undue lowering of the melting 25 point of the final structure and loss of strength at elevated temperatures.
- The mixture of particles and diluent is then heated in an oxidising atmosphere such as air, oxygen or mixtures of oxygen and inert gases at a temperature of at least about 30 400° C. but below the ignition temperature of the metal at the concentration of oxygen employed. The exact conditions for firing will depend upon the porosity of the mixture, 35 the amount of metal, the amount and kind of fluxing agent and the temperature. These interactions and variations among them will be apparent to one skilled in the art. In order to obtain substantially complete and homogenous oxidation of the metal particles, 40 the above-mentioned variables should be selected so that a spontaneous and rapid ignition does not take place, or a spontaneous and rapid reduction of the non-aluminium constituents 45 does not occur. In general at least the first stages of oxidation should be carried out at a relatively low temperature. For example, a temperature of about 700° to 1050° C. for a period of about $\frac{1}{2}$ to 48 hours can be 50 used with aluminium in combination with as little as 0.1 to 3% of an alkali metal oxide or hydroxide. The less active fluxing agents such as MgO in an amount of 0.1 to 10% will require from 1 to 72 hours at 55 temperatures of 1000° to 1350° C. or higher. It is preferred to heat at a relatively low temperature initially, until a stress bearing oxide film develops which holds the moulded shape of the aggregate during subsequent 60 further oxidation at a higher temperature. It
- is preferred that the temperature of the shapes should not exceed ambient temperature by more than 200° C. 65
- The temperature and period of the heating step are co-related functions. They will vary widely depending primarily upon the shape and concentration of the metal, the nature of the fluxing agent, the concentration of the fluxing agent and the nature of the oxidising atmosphere. In general, any temperature below the melting point of the final fired refractory body may be employed, the higher temperatures favouring a decrease in the necessary period of heating. The heating is continued for a period of time sufficient to permit oxide growth which will result in the formation of the desired crystal structure. In general, the oxidation will be carried out 70 at a temperature of from 600° to about 1000° C., when using an atmosphere of air or an atmosphere containing an equivalent amount of oxygen and a normal amount of fluxing agent. It is desirable to have a preliminary oxidation step at a temperature close to the melting point of the metal, as, for example, 16 hours at 600° C. or 2 hours at 75 700° C. In the latter case, the structure must be well supported so that a minimum of strain is put on the object and the molten aluminium is not exuded. The extent of this preliminary oxidation will also depend upon the dimensions of the metal particles in the structure. The previous remarks apply to a 5 mil diameter filament. After an initial shell of 80 oxide has been formed, then the secondary or final oxidation can be carried out at a higher temperature which may be 850° C. for 4 hours or as high as 48 hours at 1000° C. When only a thin skin of oxide is formed initially, followed by heating above the melting point of the metal, un-oxidized metal is exuded. Using this process, the alpha crystalline form of alumina (corundum) is always formed regardless of the temperature used. Unoxidized metal may be melted out of the 85 formed mass when particle morphology permits. This is an unusual phenomena which apparently results from the incompatibility of these metals and their oxides. When melted out, the metal appears in globules on the surface of the formed oxide structure from which it may be removed by abrasion, heat treatment, or the like. As much as 81% of the original metal employed may be recovered by this method (depending on the amount of metal oxidised). If a relatively thick skin of oxide is formed at the relatively low initial temperature, no metal is exuded on raising the temperature above the melting point, but a greatly increased rate of oxidation is observed. When two heating stages are 90 95 desirable, it is preferred that there be no cooling between stages to obtain the most uniform products. Alternatively, the temperature is continued for a period of time sufficient to permit oxide growth which will result in the formation of the desired crystal structure. In general, the oxidation will be carried out at a temperature of from 600° to about 1000° C., when using an atmosphere of air or an atmosphere containing an equivalent amount of oxygen and a normal amount of fluxing agent. It is desirable to have a preliminary oxidation step at a temperature close to the melting point of the metal, as, for example, 16 hours at 600° C. or 2 hours at 700° C. In the latter case, the structure must be well supported so that a minimum of strain is put on the object and the molten aluminium is not exuded. The extent of this preliminary oxidation will also depend upon the dimensions of the metal particles in the structure. The previous remarks apply to a 5 mil diameter filament. After an initial shell of oxide has been formed, then the secondary or final oxidation can be carried out at a higher temperature which may be 850° C. for 4 hours or as high as 48 hours at 1000° C. When only a thin skin of oxide is formed initially, followed by heating above the melting point of the metal, un-oxidized metal is exuded. Using this process, the alpha crystalline form of alumina (corundum) is always formed regardless of the temperature used. Unoxidized metal may be melted out of the formed mass when particle morphology permits. This is an unusual phenomena which apparently results from the incompatibility of these metals and their oxides. When melted out, the metal appears in globules on the surface of the formed oxide structure from which it may be removed by abrasion, heat treatment, or the like. As much as 81% of the original metal employed may be recovered by this method (depending on the amount of metal oxidised). If a relatively thick skin of oxide is formed at the relatively low initial temperature, no metal is exuded on raising the temperature above the melting point, but a greatly increased rate of oxidation is observed. When two heating stages are 100 105 110 115 120 125 130

- the range desired at a rate adequate to form the initial shell and thereafter provide either melting out of unoxidised metal or further oxidation at increased rate as desired.
- 5 The firing cycle (rate of heating as well as time at a given temperature) should preferably be selected so that no more than 5% of the original aluminium is exuded from the body.
- 10 Aluminium particles as previously described, mixtures of particles of aluminium and different metals, and particles of alloys of aluminium with other metals in which aluminium constitutes the major component may be used. The metal used is preferably clean and free from grease and oil. The aluminium particles should have one dimension of at least about 7 mils, (preferably 10 mils) a second dimension of at least 0.5 mil and a third dimension between 0.5 and 200 mils. For example, if spheres of aluminium are used, they must have a diameter between 7 and 200 mils (between about 3.5 and 80 mesh). Cylindrical rods as fibres must have a diameter of between 0.5 and 200 mils and a length of at least 7 mils. The length is not critical and can vary from short staple to continuous filaments.
- 15 Suitable fluxing agents for use in forming the structures of the present invention are, as defined above, any of (I) an oxide or hydroxide of a metal other than aluminium and (II) a precursor of the oxides of (I), the said oxides of (I) being of a metal from the class consisting of the alkali metals, the alkaline earth metals, vanadium, chromium, molybdenum, tungsten, copper, silver, zinc, antimony, and bismuth. The oxides and hydroxides of the alkali metals, magnesium, strontium and barium are preferred. Among suitable precursors of these materials may be mentioned the acetates, benzoates, bismuth thioglycollates, bisulphites, bisulphites, bromates, nitrates, nitrites, citrates, dithionates, ethylates, formaldehyde sulphoxylates, formates, hydrosulphites, hypochlorites, metabisulphites, methylates, oleates, oxalates, perchlorates, periodates, persulphates, salicylates, selenates, silicates, stearates, sulphates, sulphites, tartrates, and thiosulphates of the recited metals. While not "per se" within the class of useful fluxing agents, these compounds do, under conditions of the reaction, yield compounds within the above defined class. The sodium acetate, -benzoate, -bismuth thioglycollate, etc., will yield sodium oxide which is an oxide of an alkali metal.
- The suitability of the various oxides and hydroxides for use as fluxing agents can be determined by the following test:—
- 60 About 25 grams of the aluminium to be used in the process is placed in a 40 ml. alumina crucible ("Alundum"—trade mark —made by the Norton Company of Worcester, Mass.). The crucible is placed in an electric furnace to melt the aluminium, removed and the surface of the metal skimmed to remove any extraneous aluminium oxide. A pocket forms in the centre of the aluminium surface upon cooling. The major portion of a one gram sample of a powdered fluxing agent candidate (a metal oxide or hydroxide or a compound which may be expected to form a metal oxide under the conditions of the test) is placed in the pocket. A minor amount of the powder is placed so it contacts both the aluminium and the crucible at the edge. A control using powdered alumina is also prepared.
- 65 The crucibles are placed in an electrically heated furnace with an air atmosphere and heated at 1000° C. for 10 hours. The crucibles are slowly cooled and examined for a reaction. If the candidate is an effective flux at the first temperature tried, the test may be repeated at some lower temperature (e.g., 850° C.) to better classify the effective temperature. If no reaction occurs on the first trial, higher temperatures (e.g., 1300 and 1400° C. in turn) may be tried.
- 70 The most effective flux agents (class 1) are characterised by their complete disappearance, a darkening of the aluminium surface and the appearance of a black colour on the outside of the crucible. With less effective flux agents (class 2) the blackening of the crucible is not observed but (1) the surface of the aluminium is darkened and (2) the flux candidate does disappear and/or the aluminium has formed in comparison with the control. Those candidates which do not fulfil the above requirements but which do at least partially fuse into the surface of the metal are considered class 3 fluxes.
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- If all of the candidate is still loose on the surface of the aluminium it is not considered to be a fluxing agent for this process.
- The candidates must be restricted to substantially non-volatile compounds or else run under pressure in order to obtain valid results.
- Following are some fluxing agents classified by this test:

TABLE I

	Candidate	at 850° C.	at 1000° C.	at 1300° C.
5	LiOH	Class 2	Class 1	
	NaC ₂ H ₃ O ₃		Class 1	
	K ₂ C ₂ O ₄ .H ₂ O		Class 2	
	Mg(OH) ₂			Class 2
	Sr(OH) ₂ . 8H ₂ O			Class 2
	BaCO ₃		Class 1	
10	V ₂ O ₅	Class 2	Class 2	
	MoO ₃		Class 2	
	WO ₃			Class 2
	Na ₂ SiO ₃	Class 1		
	NaOH	Class 1		

- 15 The atmosphere of the firing operation must be oxidising in character. Most conveniently air is employed for this purpose. However, the process may be speeded up by enriching the atmosphere with oxygen or ozone. Other oxidising atmospheres which may be employed are argon-oxygen and helium-oxygen mixtures. It is preferred to avoid the use of nitrogen containing gases.
- 20 Where a non-porous coating upon the refractory is desired, coatings such as aluminium oxide, zirconium oxide, titanium dioxide, tantalum, a silicide, and the like may be applied by conventional metal spraying techniques.
- 25 WHAT WE CLAIM IS:—
- 30 1. A hollow particle comprising a shell of crystalline refractory material surrounding a void of 0.5 to 200 mils in diameter, the crystalline refractory being selected from the group consisting of alpha-alumina, compounds and solid solutions of alumina and at least one other metal oxide, and solid solutions of at least one metal oxide in a compound of alumina and at least one other metal oxide, there being at least 30% by weight of alumina in said crystalline refractory, the grains in said crystalline refractory exhibiting an average grain size of less than 8 microns and a density function of 0.5 to 1.0, the particle containing 0 to 81% by weight elemental aluminium, based on the weight of the particle, the aluminium, if present, being within the void and/or dispersed in the crystalline refractory.
- 35 2. A hollow particle according to claim 1 in which the shell has a thickness between 0.3 mil and the diameter of the enclosed void.
- 40 3. A hollow particle according to claim 1 or 2 which contains up to 81% residual aluminium in the central void.
- 45 4. A hollow particle according to claim
- 50 3 which contains 5 to 81% residual aluminium in the central void.
- 55 5. A hollow particle substantially as herein described with reference to the Example. 60
- 60 6. A method of making a hollow particle as claimed in claim 1 which comprises oxidising aluminium or aluminium alloy shapes in a refractory diluent in the presence of a fluxing agent in an amount equivalent to 0.02 to 20% based on the weight of aluminium present in said shapes, and, after the oxidation has been completed, separating the hollow particles from the refractory diluent, the aluminium or aluminium alloy shapes having one dimension of at least 7 mils, a second dimension of at least 0.5 mils and a third dimension of from 0.5 to 200 mils, the fluxing agent being in contact with said shapes and being selected from the oxides of the alkali metals, the alkaline earth metals, vanadium, chromium, molybdenum, tungsten, copper, silver, zinc, antimony and bismuth and precursors of said oxides, the firing conditions employed and the amount of said shapes with respect to the refractory diluent being such that during the firing and oxidation the shapes remain separated from one another. 65
- 70 7. A method according to claim 6 in which the amount of fluxing agent is from 0.2 to 5% by weight. 75
- 75 8. A method according to claim 6 or 7 in which the heating is carried out so that the temperature of the shapes does not exceed the ambient temperature by more than 200° C. 80
- 80 9. A method of making a hollow particle substantially as herein described with reference to the Example. 85
- 85 10. A method of making a hollow particle substantially as herein described with reference to the Example. 90

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